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Rheo-Optical Studies of Drawn Polypropylene Films

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For the weakly and highly drawn films of isotactic polypropylene, which form the different superstructures, birefringence relaxation and stress relaxation were measured simultaneously.

For weakly drawn films, the strain-optical coefficient increases with increasing time, while for highly drawn films, it decreases with increasing time. Time-dependent curves of the strain-optical coefficient and the relaxation modulus obtained at various temperatures could be superposed by vertical and horizontal shifts. Then, from the horizontal shift factors, activation energies for the rheo-optical and viscoelastic relaxation processes were determined. The activation energies for the highly drawn films are much higher than those for the weakly drawn films. These results indicate that the deformation mechanisms for the highly drawn films entirely differ from those for the weakly drawn films.

Relaxation experiments were also carried out for undrawn (as-quenched) polypropylene films at different strain levels ranging from 2% to 10%. The undrawn films have a different crystalline form from that of the weakly and highly drawn films. However, the difference in the crystalline form scarcely affect the relaxation processes. The nonlinearity of viscoelastic behavior observed in these relaxation experiments may be attributed to the disintegration of spherulites.

The viscoelastic and rheo-optical properties obtained for polypropylene were quite similar to those for polyethylene studied previously, showing the existence of some generalities of polyolefins.

INTRODUCTION

Rheo-optical properties of undrawn films of polyethylene and polypropylene can be well explained by the three deformation mechanisms as revealed by previous studies:¹⁾ the deformation of the spherulites as a whole, the orientation of the crystallites in the spherulites, and the orientation of amorphous chains. Rheo-optical properties for highly drawn polyethylene films are quite different from those for undrawn and weakly drawn films;²⁾ for undrawn and weakly drawn films, the strain-optical coefficient increases with increasing time, while for highly drawn films, it decreases with increasing time. The activation energies of the rheo-optical and viscoelastic relaxation processes for highly drawn films are much higher than those for undrawn and weakly drawn films. This is due to the fact that spherulites in polyethylene films are broken either partially or completely, suggesting the existence of a fourth deformation mechanism.

It was anticipated that characteristic rheo-optical and viscoelastic properties observed on polyethylene films could be observed also for other polyolefins, having the spherulitic structure in the undrawn or weakly drawn state and the fiber structure in the highly drawn state. In order to confirm this, birefringence relaxation and stress relaxation were measured simultaneously for weakly and highly drawn films of isotactic polypropylene.

To examine the effect of the crystalline form on the relaxation phenomena, experiments were also carried out with the undrawn (as-quenched) film of polypropylene, which has a

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different crystalline form from that for the heat-treated films.

Furthermore, relaxation experiments were carried out on the undrawn film at different strain levels ranging from 2% to 10% in order to examine the effect of drawing upon relaxation processes.

EXPERIMENTS

Materials

As mentioned above, weakly and highly drawn films of isotactic polypropylene were used in this study. To prepare the films, pellets of isotactic polypropylene, PLA-7409A053 produced by Mitsui Chemical Industry Co., were employed.

First, pellets of this material were placed between two aluminum plates and pressed for several seconds in a laboratory press at 210°C and a pressure of 100 kg/cm². After being released from the pressure, the melt was pressed again at 210°C and a pressure of 30 kg/cm². After 5 min, the sample, which was still contained between the aluminum plates, was plunged into an ice-water bath. As known well, the structural changes occur during the aging of polypropylene quenched from the melt.³⁻⁶⁾ Therefore, the quenched films were kept in a desiccator at 25°C for a given period of time, 24 hrs prior to the various measurements described below, so that one can minimize the fluctuation of data originating from the structural changes. The quenched film thus prepared is designated as an undrawn film.

Long strips were cut from the quenched film thus obtained, and the strips were drawn with a hand stretcher in an oven controlled at constant temperatures to obtain two kinds of drawn films. One is a weakly drawn film (drawn at 150°C) with the draw ratio of 1.3, and the other is a highly drawn film (drawn at 100°C) with the draw ratio of 3.9. The former is a film drawn uniformly before the necking point, and the latter a film drawn highly beyond the necking point. These drawn films, which were still fixed in the hand stretcher, were further heat-treated in an oven at 150°C for 45 min and then subjected to measurements. Pitch lines were marked on the films, and the separation of these lines was measured to determine the draw ratio; caution was taken to use a uniformly drawn portion of the film for the measurements.

Measurements

The density of the films was measured by the floatation method using an ethanol-water system at 30°C.

The stress relaxation and birefringence relaxation measurements were carried out with the same instrument as was used previously.⁷⁾ It consists of an Instron type tensile tester (Tensilon UTM-IV) combined with an optical system for measuring the birefringence continuously by the intensity method.

X-ray diffraction and small angle X-ray scattering measurements were carried out on a diffractometer (Model VD-1) manufactured by Shimadzu Manufacturing Co., which was described earlier.⁸⁾

RESULTS AND DISCUSSION

Characterization of the Drawn and Undrawn Films

It is well-known that isotactic polypropylene films having different crystalline forms can be prepared by changing crystallization conditions.⁹⁻¹³ The crystalline forms for three kinds of films used in this study were examined by X-ray diffraction measurements. The X-ray diffraction patterns for an undrawn film at 50°C, 70°C, and 90°C are shown in Fig. 1. The crystalline form of the undrawn film is the β -form (pseudo-hexagonal, smectic or quenched crystal) below 50°C. However, the β -form crystals are completely transformed into the α -form (monoclinic form) crystals above 90°C. Between 50°C and 90°C, both the α and β crystal forms co-exist. On the other hand, both X-ray diffraction patterns for weakly and highly drawn films showed the α crystalline form.

The density and crystallinity in weight fraction was evaluated from the density, using

$$x_c = \frac{\rho_c}{\rho} \left(\frac{\rho - \rho_a}{\rho_c - \rho_a} \right) \times 100 (\%), \quad (1)$$

where ρ is the density of the film, and ρ_a and ρ_c are, respectively, the densities for the amorphous and crystalline phases. ρ_a was assumed to be 0.854,¹⁴ and ρ_c for the α and β forms to be 0.938¹⁴ and 0.910,^{15,16} respectively.

The average degree of orientation of the crystals can be represented in terms of orientation function, f defined by Hermans.¹⁷ The average orientations of the crystallographic b- and c-axes were determined from azimuthal scans of the (040) and (110) reflections, respectively, using the following equation proposed by Wilchinsky.¹⁸

$$f_c = -1.099 f_{110} - 0.901 f_{040} \quad (2)$$

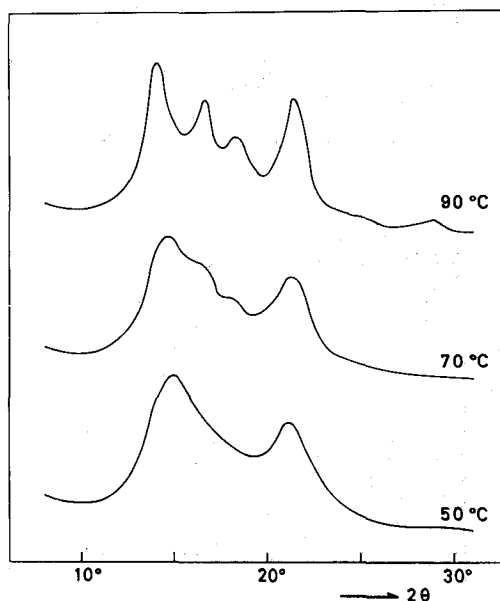
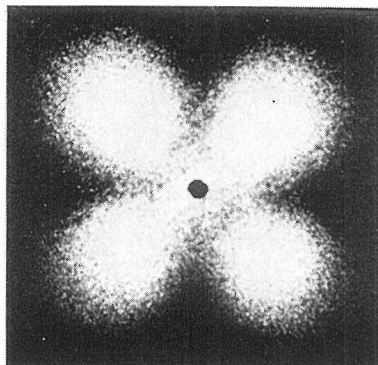
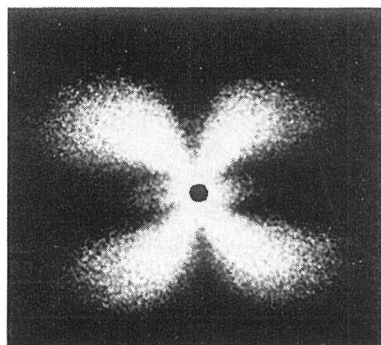


Fig. 1. The pattern of X-ray diffractions for the undrawn film of polypropylene, measured at 50°, 70°, and 90°C.

Table I. Morphological Data for the Undrawn and Drawn Films

	Drawn Films		Undrawn Films (quenched)
	weakly	highly	
Draw Ratio	1.3	3.9	1.0
Crystalline Form	α ($20^\circ < T < 120^\circ\text{C}$)	α ($20^\circ < T < 140^\circ\text{C}$)	β ($T < 50^\circ\text{C}$) α & β ($50^\circ < T < 90^\circ\text{C}$) α ($T > 90^\circ\text{C}$)
Density (g/cm^3)	0.910	0.911	0.833
Crystallinity (wt %)	68	70	54
Orientation Functions			
f_c	0.26	0.91	0
f_b	-0.16	-0.47	0
f_{a^*}	-0.10	-0.44	0
Long Period (\AA)	—	280	—

Undrawn

Drawn $\lambda = 1.3$ 

D.D.

Fig. 2. The H_v -light scattering patterns for the undrawn and weakly drawn ($\lambda=1.3$) films.

The orientation function for the a^* -axis of the (a^*, b, c) orthorhombic system, f_{a^*} , was assumed to be almost equal to that for the a -axis of the (a, b, c) monoclinic crystal system and calculated by

$$f_{a^*} = -f_b - f_c \quad (f_b = f_{040}) \quad (3)$$

As is shown in Table I, for the weakly drawn films, the b -axis orients more perpendicular to the stretching direction than the a^* -axis. This indicates that the c -axis orients to the stretching direction by tilting or twisting of crystallites about the lamella axis (*i.e.* the a -axis). In other words, it indicates the existence of spherulitic structures in the films. This orientation behavior is similar to that of the b - and a -axes for polyethylene films,¹⁹⁾ though the a -axis orients more perpendicular to the stretching direction than the c -axis. (The tangential axis of spherulite for polyethylene is the b -axis.) For highly drawn films, f_{a^*} is almost the same as f_b , suggesting the axial orientation.

The long period of the highly drawn films, estimated from the small angle X-ray scattering by using Bragg condition, is 280 Å.

As is evident from Fig. 2, the H_v -light scattering patterns for the undrawn and weakly drawn films are the so-called "four-leaf clover" patterns, which have been shown to arise from the spherulitic structure. By the method²⁰⁾ proposed by Stein and Rhodes, the radius of the spherulite can be estimated to be about 6 μ . For the weakly drawn film, it is seen that the spherulites are deformed a little.

The stress-strain curves and the birefringence-strain curves obtained for all the samples are given in Figs. 3(a) and 3(b). To obtain these curves, the film was elongated at a constant speed of 10%/min at room temperature. As is evident from Fig. 3(a), the initial slopes of the stress-strain curves and yield stresses differ from sample to sample. More remarkable difference can be seen in the birefringence-strain curves in Fig. 3(b). For the undrawn and weakly drawn ($\lambda=1.3$) films, negative birefringence is observed at low

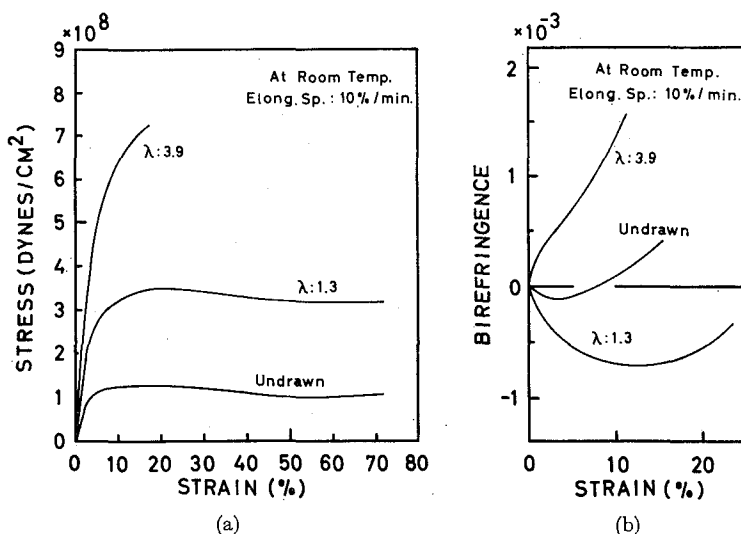


Fig. 3. The stress-strain curves (a) and the birefringence-strain curves (b) for the undrawn and drawn films, measured at a constant speed of 10%/min at a room temperature.

strains, while for the highly drawn ($\lambda=3.9$) film, positive birefringence is always observed.

The negative birefringence may be caused by the affine deformation of spherulite as a whole; the lamellae (or the a -axis) orients to the stretching direction. The birefringence at any strain for the weakly drawn film is lower than that for the undrawn film. This indicates that more solid spherulites may be formed in the weakly drawn film in the process of heat-treatment. Positive birefringence at any strain level for the highly drawn film can be understood by the fact that its spherulitic structure is completely broken during the preparation of the films.

Stress Relaxation and Birefringence Relaxation

Several strips, 5 cm in length and 1.5 cm in width, were cut from sample films and used for relaxation measurements. The strip was first elongated at a constant speed of 100%/min to various extents (about 2% for weakly drawn films and about 5% for highly drawn films). The application of a little higher strain (about 5%) to the highly drawn films was to measure the birefringence as precisely as possible.

Here, the strain γ is defined as (draw ratio) \times (elongation)/(initial length). The results of stress relaxation for weakly ($\lambda=1.3$) and highly ($\lambda=3.9$) drawn films obtained at temperatures between 20°C and 140°C, are shown in Figs. 4 and 5, respectively. As is evident from these figures, the relaxation modulus $E(t)$ (=stress/strain) for both the samples decreases with increasing time, but the relaxation rate is somewhat lower for the highly drawn film than for the weakly drawn one.

The birefringence relaxation data corresponding to the stress relaxation data shown in Figs. 4 and 5 are given in Figs. 6 and 7. It is clear from these figures that the birefringence relaxation behavior for the weakly drawn film differs markedly from that for the highly drawn one. Namely, the strain-optical coefficient Δ/γ for the weakly drawn film increases with increasing time, while that for the highly drawn films decreases.

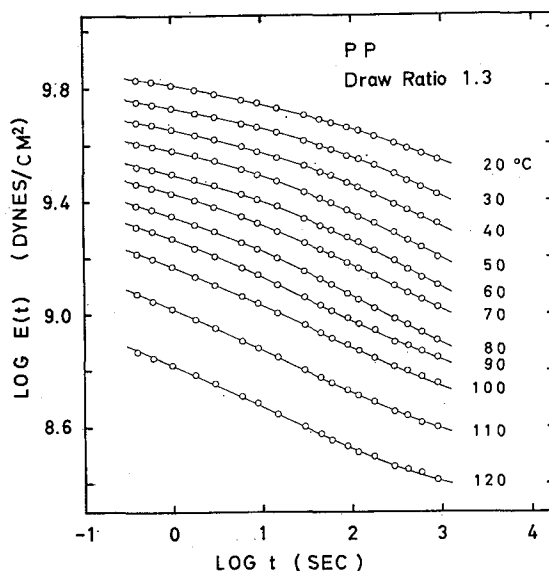


Fig. 4. The variation of relaxation modulus $E(t)$ with time t for the weakly drawn films ($\lambda=1.3$) at various temperatures.

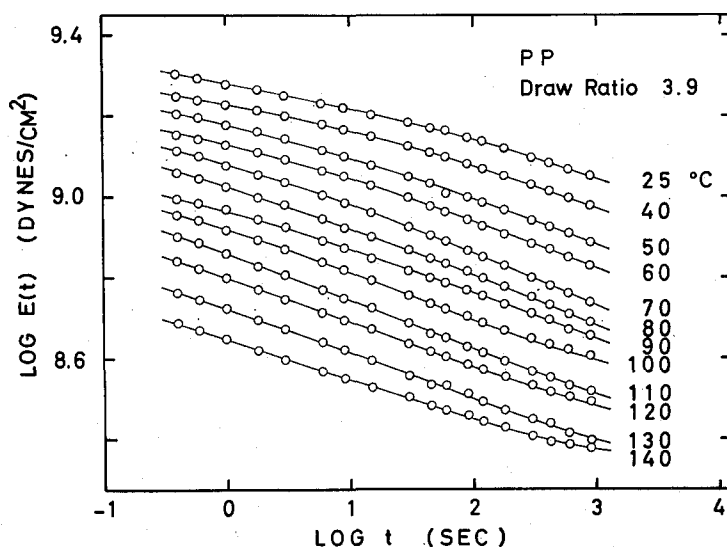


Fig. 5. The variation of relaxation modulus $E(t)$ with time t for the highly drawn films ($\lambda=3.9$) at various temperatures.

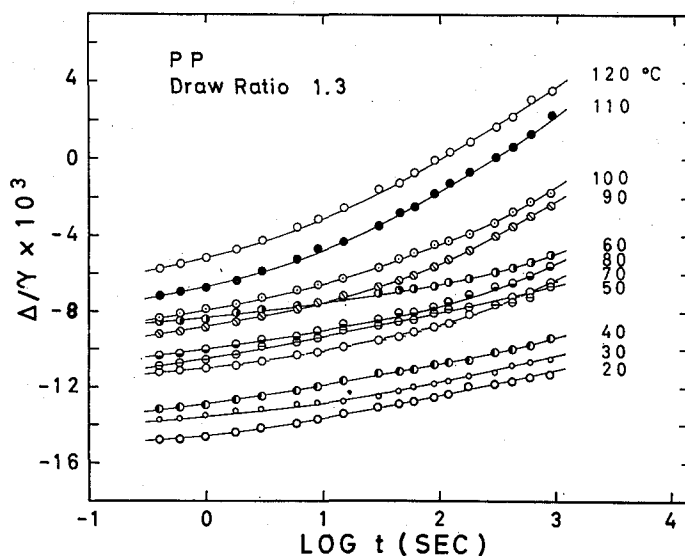


Fig. 6. The variation of strain-optical coefficient Δ/γ with time t for the weakly drawn films ($\lambda=1.3$) at various temperatures.

Negative values of Δ/γ for the weakly drawn film are due to the fact that birefringence decreases by rapid deformation of the spherulites though the film shows a positive birefringence before application of initial strain. The birefringence increases with increasing time, indicating that the c -axis of the crystallites in a spherulite orients gradually to the stretching direction, as discussed above. The relaxation time for this process is long enough to be observed in the relaxation measurements.

The time-temperature superposition method was applied to the stress relaxation curves

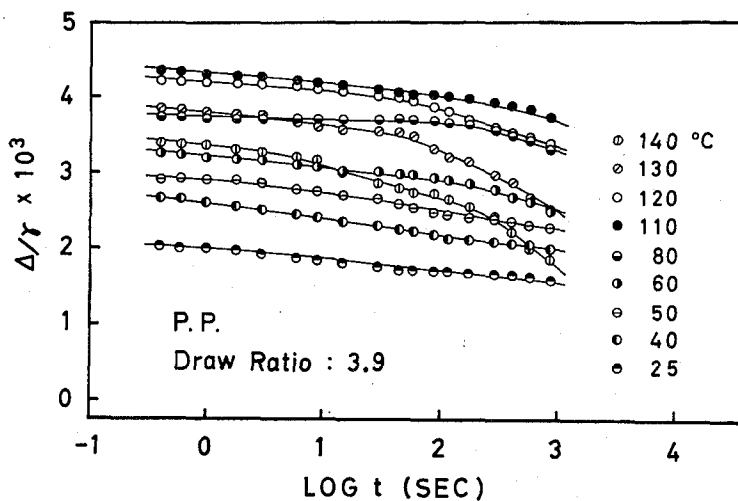


Fig. 7. The variation of strain-optical coefficient Δ/γ with time t for the highly drawn films ($\lambda=3.9$) at various temperatures.

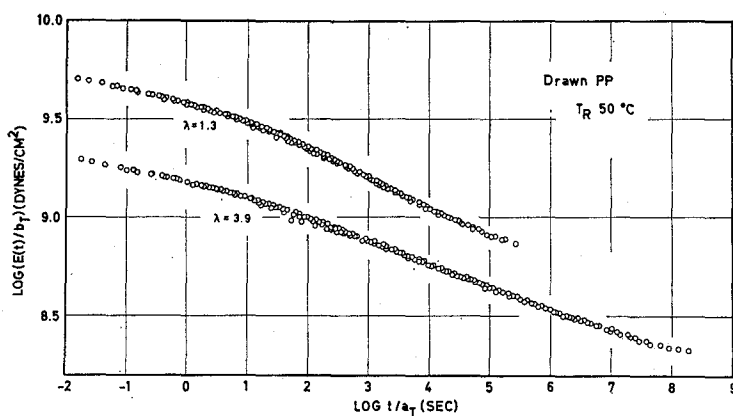


Fig. 8. Master curves of relaxation modulus for the weakly ($\lambda=1.3$) and highly ($\lambda=3.9$) drawn films.

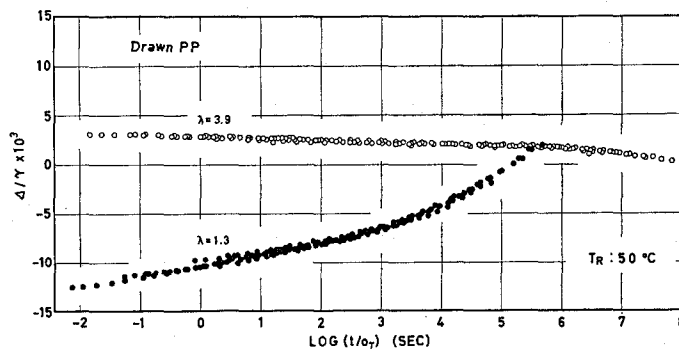


Fig. 9. Master curves of strain-optical coefficient for the weakly ($\lambda=1.3$) and highly ($\lambda=3.9$) drawn films.

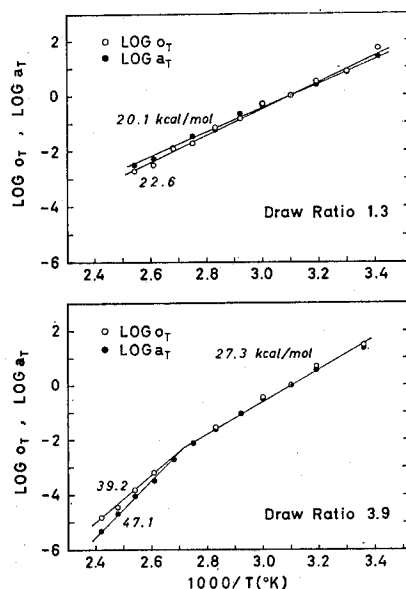


Fig. 10. Viscoelastic and rheo-optical horizontal shift factors, a_T and o_T , plotted against $1/T$ for the weakly ($\lambda=1.3$) and highly ($\lambda=3.9$) drawn films.

shown in Figs. 4 and 5 as well as to the birefringence relaxation curves shown in Figs. 6 and 7. In order to obtain smooth master curves, vertical shifts were required as well as horizontal shifts. The master curves of the relaxation modulus $E(t)$ for the weakly and highly drawn films are shown in Fig. 8. The corresponding master curves of the strain-optical coefficient Δ/γ for the same samples are shown in Fig. 9. It should be mentioned here that the curves for the weakly and highly drawn films show quite different tendencies.

The logarithm of rheo-optical and mechanical horizontal shift factors, o_T and a_T , are plotted against reciprocal absolute temperature in Fig. 10. For the weakly drawn film, both the $\log o_T$ vs. $1/T$ and $\log a_T$ vs. $1/T$ plots are given by respective straight lines. The slope of the curves gives the activation energy ΔH for the rheo-optical or mechanical relaxation process; 22.6 kcal/mole and 20.1 kcal/mole were evaluated for the rheo-optical and mechanical relaxation processes, respectively. On the other hand, for the highly drawn film, the plots are approximated by two straight lines. Activation energies evaluated from their slopes are given on the curves in Fig. 10. The lower values of ΔH at lower temperatures for the rheo-optical and mechanical relaxation processes are the same (27.3 kcal/mole), and those at higher temperatures are about 40 kcal/mole, though ΔH for the mechanical relaxation processes is a little higher than that for the rheo-optical relaxation process. Thus, the activation energies for the highly drawn film are much higher than those for the weakly drawn film. This difference in the activation energies between the weakly and highly drawn films could be anticipated from the fact that the master curves of Δ/γ for the weakly and highly drawn films in Fig. 9 are quite different from each other. In other words, the rheo-optical properties, and hence the underlying deformation or orientation mechanisms, for the weakly drawn film are quite different from those for the highly drawn film.

The results can be well-explained by the following picture: when a spherulite in

weakly drawn film deforms as a whole upon sudden stretching, various internal motions occur. Most lamellae are subjected mainly to stretching in the direction of their length, as well as to bending forward the direction of the stretching. By such a process, the crystal c -axis orients perpendicular to the stretching direction. As time elapses, this orientation relaxes, and the c -axis orients to the direction of stretching to increase the birefringence Δ with increasing time. This relaxation mechanism must be the same as the α_1 -loss mechanism observed in polyethylene.^{1,21)}

In the case of highly drawn film, which has fiber structure, the spherulites are completely broken. Therefore, the deformation mechanism observed on weakly drawn film disappears almost entirely. In other words, the decrease in birefringence with time should be due to a new relaxation mechanism, which has not been observed on undrawn or weakly drawn films. In this case, amorphous molecular chains and crystallites are oriented in the stretching direction upon sudden stretching. As time elapses, this orientation relaxes, and the birefringence also simply relaxes. It cannot be confirmed that such a relaxation process occurs only in the crystalline region. Such process would always be accompanied by the relaxation of amorphous chains. The activation energy for this type of process is about 30–40 kcal/mole, as mentioned above, and is much higher than that of about 20–25 kcal/mole which is characteristic of the crystalline orientation process for undrawn and weakly drawn films.

Relaxation for Undrawn Films under Large Strains

Relaxation measurements following the application of different strain levels (2, 5, and 10%) were also carried out with the undrawn film at temperatures between 20° and 140°C. The crystalline form for the undrawn film is different from that for the drawn films as mentioned before. In this strain range, the films were elongated uniformly, showing no necking, but the stress-strain behavior was nonlinear at strains of 5 and 10%.

Master curves of the relaxation modulus $E(t)$ and the strain-optical coefficient Δ/γ , obtained by time-temperature superposition, are shown in Figs. 11 and 12. Although it is not clear from the figures, the superposition is not so satisfactory as in the case of poly-

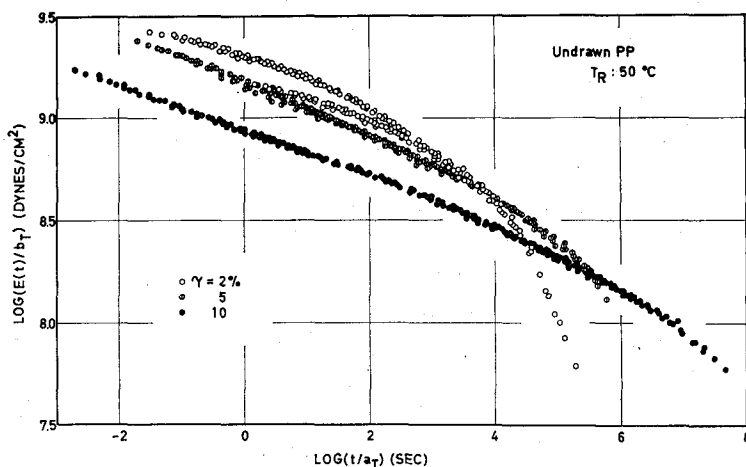


Fig. 11. Master curves of relaxation modulus for the undrawn films measured at strain levels of 2, 5, and 10%.

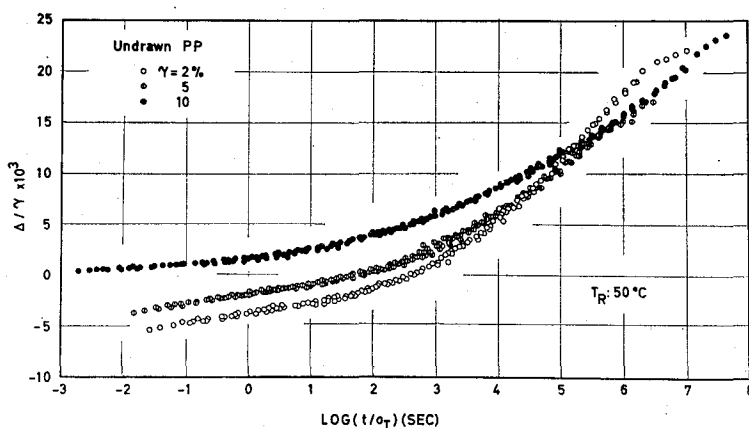


Fig. 12. Master curves of the strain-optical coefficient for the undrawn films measured at strain levels of 2, 5, and 10%.

ethylene, and both the master curves of Δ/γ and $E(t)$ are not smooth, especially at strain level of 2%. This may be attributed partially to the fact that the β form of polypropylene transforms to the α form at around 50°C and partially to the variation of the stiffness of the superstructure with temperature.

In spite of the fact that the crystalline form of the undrawn film differs from that of the weakly drawn film, both the master curves of $E(t)$ and Δ/γ for the undrawn film are very similar to those for the weakly drawn film. This suggests that the relaxation process for the undrawn films is almost the same as that for the weakly drawn film. That is, the relaxation processes appearing in this study are governed mainly by the nature of superstructure rather than by the crystalline form.

As is evident from Fig. 12, the rate of increase in the strain-optical coefficient with time becomes low as the strain level increases. At higher levels of strain, spherulites in the sample film are broken to a great extent by a sudden deformation, and this lessens the increase in birefringence caused by the crystalline orientation. The breaking of the spherulites under large strains seems to be one of prime factors in producing the nonlinear viscoelastic behavior. The authors are studying further about this nonlinear effect by dynamic viscoelastic experiments.

The activation energies for the relaxation processes were also evaluated from the temperature dependences of the viscoelastic and the rheo-optical horizontal shift factors. In the temperature region below 50°C, where the β crystalline form is dominant activation energies for the rheo-optical and viscoelastic processes were the same; 15.7 kcal/mole for the strain level of 2%, 20.8 kcal/mole for 5%, and 32.8 kcal/mole for 10%. The increase in activation energy with the strain level may be due to the involvement of other relaxation process with higher activation energy associated with the partial disintegration of the spherulites.

Summarizing the above results, the following conclusions are drawn:

(1) The rheo-optical and viscoelastic mechanisms are mainly governed by the nature of the superstructure. The differences in the crystalline form and stiffness of spherulites, brought about the aging or heat treatment, affect only the mobility of crystallites and amorphous chains, and hence the activation energy of the relaxation process.

(2) Nonlinearity in viscoelastic and rheo-optical behaviors for the undrawn film can be attributed mainly to the breaking of spherulites under large strains.

These conclusions obtained for the undrawn and drawn polypropylene films are quite similar to those obtained for polyethylene films.²⁾ It would be general also for the polyolefins, in which spherulitic structure is formed in the undrawn and weakly drawn state and fiber structure in the highly drawn state.

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